



## On the promotional effect of Cu on Pt for hydrazine electrooxidation in alkaline medium

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### ABSTRACT

Pt/C and PtCu/C electrocatalysts with nominal Pt:Cu atomic ratios of 75:25, 50:50, and 25:75 were prepared using  $N_2H_4$  as reducing agent and carbon black Vulcan XC-72R as support. The obtained materials were physically characterized by X-ray diffraction, Energy-Dispersive X-ray analysis, Transmission Electron Microscopy images, X-ray Photoelectron Spectroscopy (XPS), and Temperature-Programmed Reduction analysis. Cyclic voltammetry, linear sweep voltammetry, and chronoamperometry (TPR) measurements were carried out in a three-electrode glass cell to evaluate the electrochemical activity towards hydrazine electrooxidation in alkaline medium along with single-cell direct hydrazine fuel cell (DHFC) tests. The actual composition of the electrocatalysts evidenced a slightly lower Cu fraction compared to the nominal one. The X-ray diffractograms of the electrocatalysts showed the typical face-centered cubic structure of Pt alloys, with the highest fraction of Cu alloyed to Pt being achieved with the almost equiatomic catalyst. An important fraction of the remaining non-alloyed Cu is in the form of a copper oxide, as evidenced by XPS and TPR measurements. The electrochemical tests evidenced that the coexistence of part of the Cu alloyed with Pt and copper oxide achieved in the PtCu/C electrocatalysts enhances the performance compared to Pt/C. In particular, the optimum formulation is attained by the  $Pt_{53}Cu_{47}/C$  electrocatalyst, allowing maximization of the electrocatalytic activity towards hydrazine electrooxidation and the single-cell performance at 60 and 80 °C.

### 1. Introduction

Due to operational and infrastructure problems related to the use of hydrogen as fuel in proton exchange membrane fuel cells (PEMFCs) [1–3], liquid fuels have been proposed as an alternative. Their direct oxidation avoids the need to install an onboard reformat system, as proposed for the alcohols [4]. Within the group of liquid fuels, hydrazine appears as a promising candidate. Its synthesis is relatively simple and can be combined with the mass production of ammonia, resulting in a relatively economical fuel.

Hydrazine monohydrate [ $N_2H_4 \cdot H_2O$ , normal boiling point (NBP) = 121 °C] can be used directly as fuel in PEMFCs: it shows less volatility than the conventional alcohols used in fuel cells (methanol, NBP = 65 °C; ethanol, NBP = 78 °C), non-flammability, and a melting temperature of approximately –50 °C, which makes its use in cold

countries feasible [5]. According to the International Agency for Research on Cancer (IARC), hydrazine monohydrate is classified as 2B, like gasoline, so the safety protocols used for handling gasoline may be maintained for hydrazine monohydrate [5]. Furthermore, in Direct Hydrazine Fuel Cells (DHFCs), nitrogen and water are the final by-products obtained. Furthermore, a high cell voltage with a potential maximum cell voltage of 1.62 V can theoretically be produced by hydrazine electrooxidation (HYEO) and oxygen electroreduction. DHFCs have been operated under acidic and alkaline conditions. In acidic medium, noble metals such as platinum and palladium are generally used [6]. In alkaline medium, other metals such as rhodium, ruthenium, gold, and silver and common metals such as copper also present electrocatalytic activity towards HYEO and have been tested with success in DHFCs [6,7]. Leading investigations have been presented by the Daihatsu Motor Company (Japan) in partnership with Prof. Atanasov's

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research group and Los Alamos National Laboratory (USA). They present promising electrochemical results accompanied by extensive physico-chemical characterizations with Pt-free electrocatalysts based on Ni (NiMo/C [8] and NiO/Nb<sub>2</sub>O<sub>5</sub>/C [9]) in the search for highly active and selective (minimizing the formation of NH<sub>3</sub>) material. Furthermore, Sakamoto et al. [10] recently proposed a multi-step reaction DHFC, a promising alternative offering a stable power output over long operating periods. In this approach, both hydrazine and hydrogen (from the chemical decomposition of hydrazine) are used as fuel, allowing a significant reduction of the hydrazine crossover and the formation of significant products from the combination of hydrazine and oxygen in the cathode.

Platinum is considered as a reference material for HYEEO. Compton and Aldous [11] showed that in the presence of activated or oxidized Pt, the Pt surface becomes more active, with a significant reduction in the onset potential. On the other hand, as mentioned above, copper, which is more abundant and affordable, is an active material for HYEEO, especially in alkaline medium, in both the metallic [12–16] and oxidized forms [16–19]. Moreover, a very recent study presented by de Oliveira et al. [20] demonstrated the importance of the presence of oxidized sites (NiO<sub>x</sub>) adjacent to Pt to promote the HYEEO through a bifunctional effect. Furthermore, the formation of a PtCu alloy can also lead to changes in the Pt electronic environment that modify the binding energy of the reactants on the catalytic active sites (electronic effect) [21]. In this sense, Karaca et al. [22] have evidenced a significant enhancement when using a PtCu alloy for the hydrolytic dehydrogenation of ammonia and hydrazine borane. Therefore, the preparation of a PtCu electrocatalyst may be of interest for DHFCs if the bifunctional and electronic effects of the formation of the bimetallic alloy and the presence of copper oxides could be combined.

With this background, this paper shows the results of a study in which carbon-supported PtCu bimetallic electrocatalysts with different Pt:Cu atomic proportions have been prepared by chemical reduction with hydrazine. The catalysts have been physically characterized by X-Ray Diffraction (XRD), Energy-Dispersive X-Ray (EDX) spectroscopy, Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), and Temperature-Programmed Reduction (TPR) to attain a complete description of the prepared materials. The physical and morphological information obtained is subsequently used to assist in interpreting the electrochemical activity for HYEEO, which is evaluated by linear sweep voltammetry (LSV) and chronoamperometric studies (CA) in a three-electrode glass cell, and by application as anodes in an alkaline single-cell DHFC.

## 2. Experimental

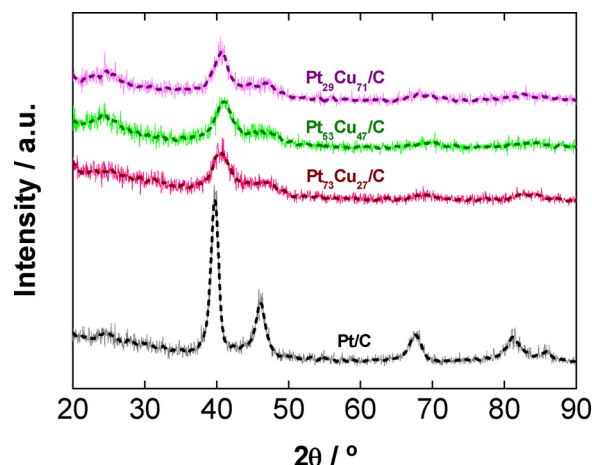
Four electrocatalysts with a nominal metal loading of 20 wt.%, Pt, Pt<sub>73</sub>Cu<sub>27</sub>/C, Pt<sub>53</sub>Cu<sub>47</sub>/C, and Pt<sub>29</sub>Cu<sub>71</sub>/C, deposited on carbon black (Vulcan XC-72R, Cabot Corp.), were prepared by chemical reduction with hydrazine (CRH, N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, Sigma Aldrich). The chemicals H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Aldrich) and CuCl<sub>2</sub>·2H<sub>2</sub>O (Synth) were used as metal sources, while 2-propanol (Synth) and ultra-pure water (Milli-Q, Millipore) were used as solvents. For the preparation of 500 mg of electrocatalysts, the required metal salts were dissolved in 200 mL of a water/2-propanol (90/10 v/v) solution. Subsequently, 400 mg of the carbon support was added to solution and the resulting mixture was sonicated for 30 min. After this time had elapsed, the mixture was placed under vigorous stirring and a reducing solution (50 mL of 2:1 v/v of water/hydrazine) was added at once. The reaction medium was kept under stirring for 30 min at room temperature. Finally, the mixture was filtered and the obtained material was washed with excess water and dried at 70 °C for 2 h.

The Pt:Cu atomic ratios of the bulk of the electrocatalysts were obtained by EDX analysis using a JEOL 2100 scanning electron microscope with a 15-keV electron beam. The XRD analyses were carried out in a Rigaku model D8 Focus diffractometer using Cu K<sub>α</sub> radiation ( $\lambda = 0.15406$  nm). The diffractograms were recorded with  $2\theta$  angles in the range of 20–90° (0.05° step, 0.5° min<sup>−1</sup>). The average crystallite ( $d$ )

**Table 1**

Pt:Cu atomic ratios for PtCu/C electrocatalysts and weight percentages of metal and carbon loadings for PtCu/C and Pt/C electrocatalysts obtained by EDX.

Electrocatalyst	Carbon loading (wt. %)	Metal loading (wt. %)	Pt:Cu atomic ratio	
			Nominal	EDX
Pt/C	80	20	–	–
Pt <sub>73</sub> Cu <sub>27</sub> /C	79	21	75:25	73:27
Pt <sub>53</sub> Cu <sub>47</sub> /C	82	18	50:50	53:47
Pt <sub>29</sub> Cu <sub>71</sub> /C	84	16	25:75	29:71



**Fig. 1.** X-ray diffractograms of Pt/C and PtCu/C electrocatalysts.

**Table 2**

Average crystallite sizes and lattice parameters of Pt/C and PtCu/C electrocatalysts obtained by XRD and average particle size obtained from TEM images.

Electrocatalyst	Crystallite size (nm)	Lattice parameter (nm)	Cu fraction in the alloy	Fraction of Cu alloyed	Average particle size (nm)
Pt/C	4.6	0.391	–	–	8.1
Pt <sub>73</sub> Cu <sub>27</sub> /C	2.1	0.387	0.174	0.427	7.4
Pt <sub>53</sub> Cu <sub>47</sub> /C	2.3	0.382	0.337	0.428	7.1
Pt <sub>29</sub> Cu <sub>71</sub> /C	2.5	0.386	0.207	0.107	7.3

size was obtained by the application of Scherrer's Eq. (1), where  $K$  is a particle-shape-dependent constant (0.9 for spherical particles),  $\lambda$  is the wavelength of the incident radiation (Cu K<sub>α</sub>),  $\theta$  is the angle of the (hkl) peak, and  $\beta_{(2\theta)}$  is the width in radians of the diffraction peak at half height.

$$d = \frac{K\lambda}{\beta_{(2\theta)} \cos \theta} \quad (1)$$

TEM analysis was performed using a JEOL 2100 microscope operating at 200 kV with point-to-point resolution of 0.19 Å. The particle size distribution was estimated from observations of at least 300 particles in different images. The average particle size,  $D$ , was calculated according to Eq. (2), where  $n_i$  represents the number of particles of diameter  $D_i$ . The sample holder was composed of a gold grid covered by Lacey carbon (EMS).

$$D = \frac{\sum_i n_i D_i}{\sum_i n_i} \quad (2)$$

XPS measurements were carried out using a Physical Electronics (PHI) 5800-01 spectrometer. A monochromatic Al K<sub>α</sub> X-ray source was used at a power of 350 W. Spectra were obtained with pass energies of 58.7 eV for elemental analysis and 11.75 eV for determination of the

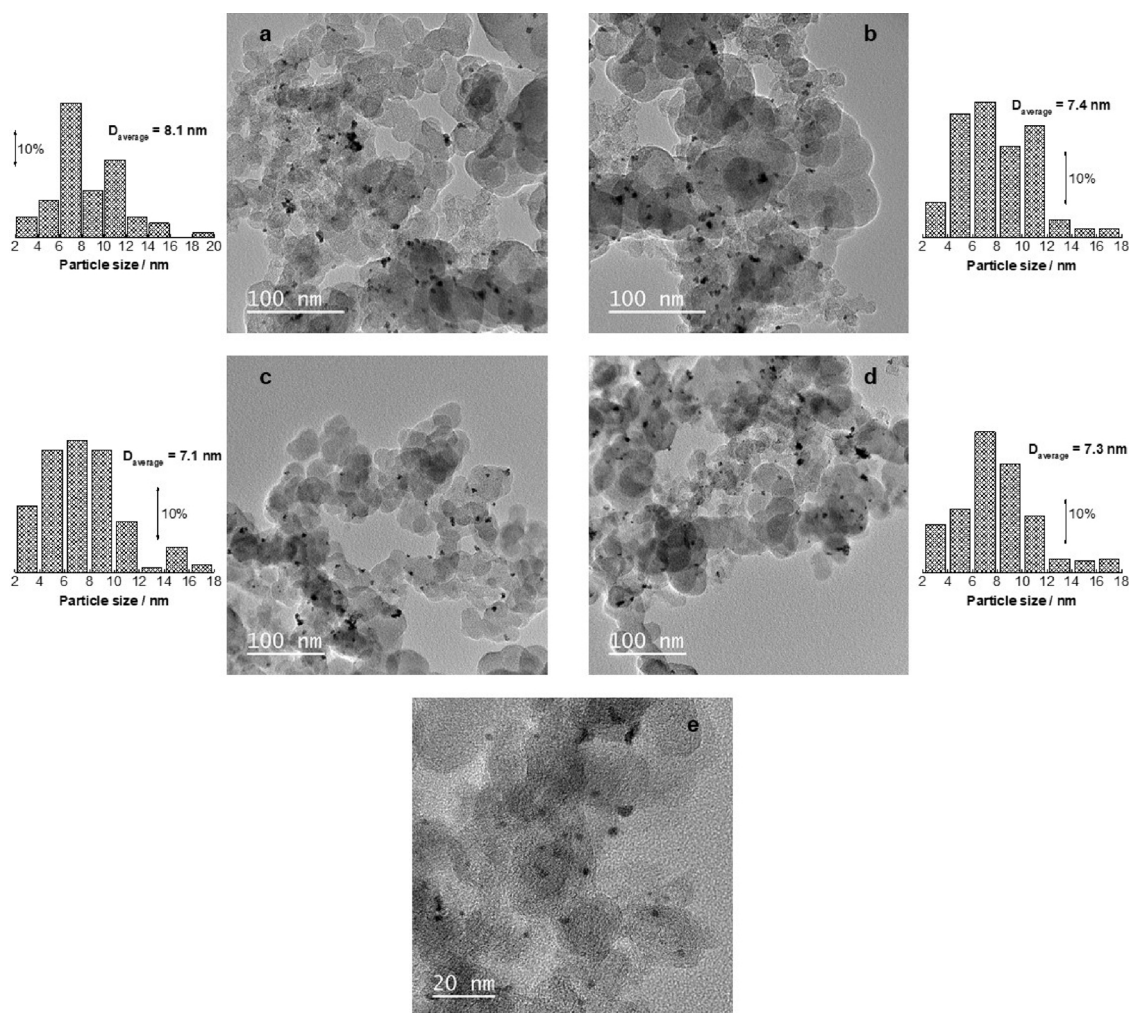


Fig. 2. TEM images of the electrocatalysts: a) Pt/C, b) Pt<sub>73</sub>Cu<sub>27</sub>/C, c) Pt<sub>53</sub>Cu<sub>47</sub>/C, and d) Pt<sub>29</sub>Cu<sub>71</sub>/C and e) high-resolution image of the Pt<sub>53</sub>Cu<sub>47</sub>/C.

oxidation states. The pressure in the analysis chamber of the spectrometer was  $10^{-9}$  torr during measurements. The Ag 3d<sub>5/2</sub> peak of an Ag foil was used, after argon sputtering, to check the calibration of the binding energy scale. Quantitative evaluation of each peak was performed by dividing the integrated peak area by atomic sensitivity factors, which were calculated from the ionization cross-sections, the mean free electron escape depth, and the measured transmission functions of the spectrometer. XPS data were interpreted by using the online library of oxidation states implemented in PHI MultiPak 6.1 software and the PHI *Handbook of X-ray Photoelectron Spectroscopy* [23]. By using this technique, it is possible to obtain information about the outermost layers of the metallic nanoparticles, which are fundamental for the electrocatalytic activity [24].

The TPR profiles were obtained under hydrogen atmosphere in a linear quartz microreactor (i.d. = 4 mm) fed with a 5-vol.% H<sub>2</sub>/Ar purified carrier at a rate of 30 sccm. The experiments were carried out in the range of 25–900 °C at a heating rate of 10 °C min<sup>-1</sup>. The weight of sample used was approximately 15 mg. The hydrogen consumption was monitored by a thermal conductivity detector calibrated against the peak area of known amounts of CuO. The resultant TPR data were highly reproducible in terms of the positions of maxima ( $\pm 2$  °C) and extent of H<sub>2</sub> consumption ( $\pm 3$  °C).

Electrochemical studies were carried out using the ultra-thin coating technique. Electrochemical measurements were performed in a three-electrode cell using a platinumized Pt plate as counter electrode, an Hg/HgO/KOH electrode as reference electrode, and a reticulated vitreous carbon (RVC) working electrode (5 mm in diameter). This

electrode was prepared by dispersing 1 mg of the electrocatalysts in 1 mL of 2-propanol. The mixture was sonicated for 10 min; then, with the aid of a chromatographic syringe, 20  $\mu$ L of the dispersion was transferred onto the surface of the previously polished RVC electrode. The experiments were performed using a  $\mu$ -Autolab (model Type III) potentiostat/galvanostat coupled to a personal computer and General Purpose Electrochemical System (GPES) software. CV measurements were performed in a 1.0 mol L<sup>-1</sup> KOH solution at a scan rate of 10 mV s<sup>-1</sup>. The study of H<sub>2</sub> was performed at room temperature by LSV and chronoamperometry (for 30 min) at 0.024 V versus Hg/HgO in a solution of 1.0 mol L<sup>-1</sup> hydrazine in 1.0 mol L<sup>-1</sup> KOH. The current values obtained were Pt-mass normalized.

DHFC tests were performed on a single cell. Electrodes with an active area of 4 cm<sup>2</sup> were prepared as follows. For the anodes, a catalytic ink containing Pt/C or PtCu/C electrocatalyst (catalyst loading of 0.5 mg Pt cm<sup>-2</sup> for both monometallic and bimetallic materials) and Nafion® emulsion [5 wt.% emulsion in a mixture of aliphatic alcohols (IonPower), forming 10 wt.% of the total catalyst] was brush-painted onto a carbon cloth (Zoltec PX30) diffusion layer. In a similar way, cathodes were prepared using 20 wt.% Pt/C (BASF fuel cells) using a Pt loading of 1 mg cm<sup>-2</sup>. The membrane electrode assemblies were prepared by hot pressing the anode and cathode onto a pretreated Tokuyama membrane (24 h in 1 mol L<sup>-1</sup> KOH solution) at 60 °C for 3 min under a pressure of 40.8 kgf cm<sup>-2</sup>. Electrical performances were determined from polarization and power density curves using a single cell at 60 and 80 °C. The fuel was delivered at 2.4 mL min<sup>-1</sup> through the anode and pure oxygen flow was regulated at 30 sccm for the



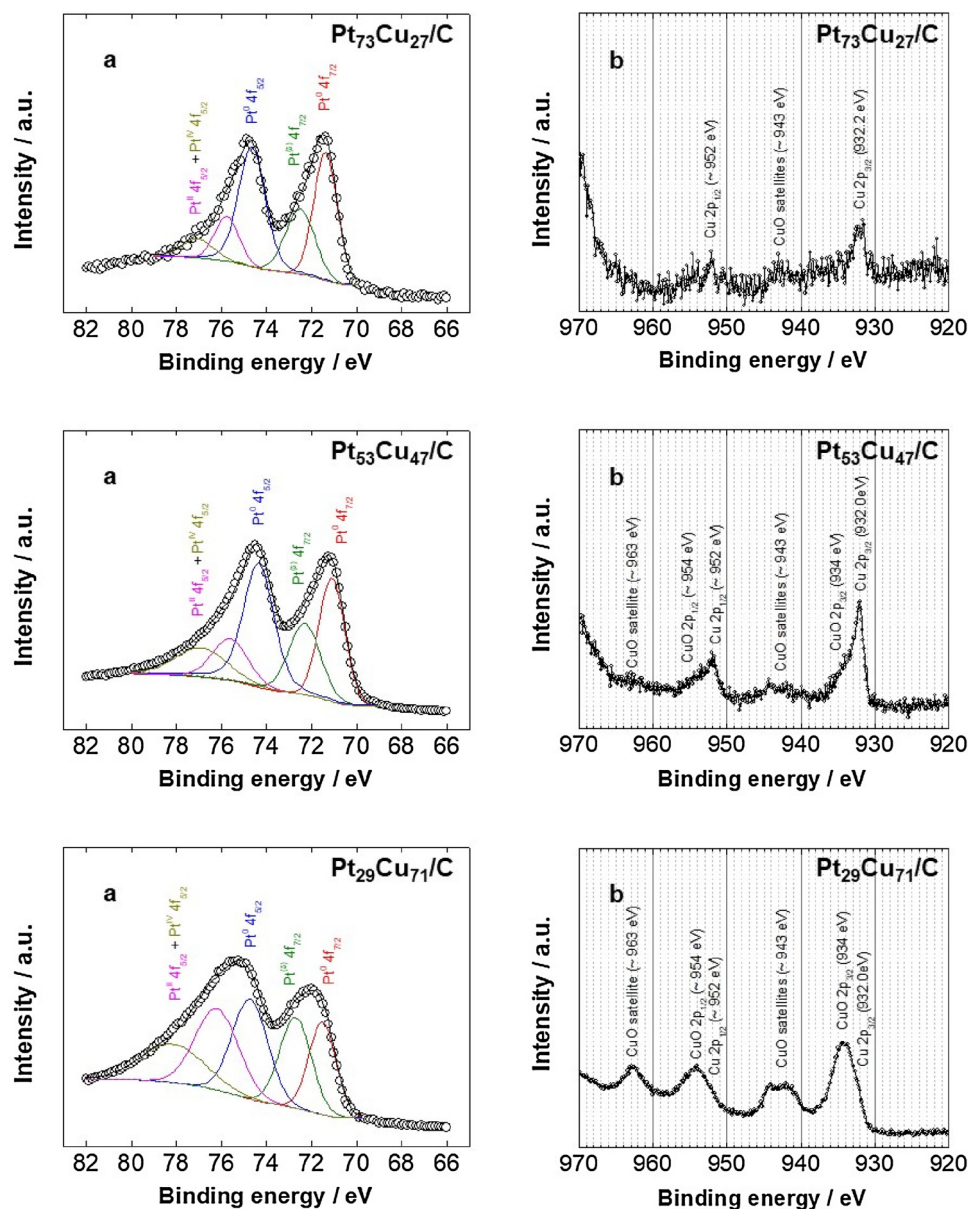


Fig. 3. Pt 4f (a) and Cu 2p (b) XPS spectra of the different electrocatalysts.

Table 3

Surface elemental analysis results for PtCu/C electrocatalysts based on XPS data.

Electrocatalyst	Atomic percentage (%)		Platinum oxidation state (%)	
	Pt	Cu	Pt (0)	Pt (δ+)
Pt <sub>73</sub> Cu <sub>27</sub> /C	77	23	56	44
Pt <sub>53</sub> Cu <sub>47</sub> /C	60	40	57	43
Pt <sub>29</sub> Cu <sub>71</sub> /C	41	59	44	56

cathode.

### 3. Results and discussion

In order to assess the actual Pt:Cu ratios in the electrocatalysts, EDX analyses were carried out. Table 1 lists the corresponding results. In general, the obtained Pt:Cu atomic ratios were similar to the nominal values, with the exception of the electrocatalysts with the highest Cu fraction (Pt:Cu ratio of 25:75), where a higher Pt fraction of 29:71 was

obtained. A possible reason for this will be discussed later on, based on the smaller fraction of Cu alloyed to Pt and greater presence of copper oxides, whose anchorage on the carbon support is partially limited. This could also explain the higher deviation of the metallic content of the catalyst on the carbon support with respect to the nominal 20%; that is, the higher the Cu fraction, the greater the deviation. From now on, the electrocatalysts will be referred to by the actual compositions.

Fig. 1 shows the X-ray diffractograms of the Pt/C and PtCu/C electrocatalysts. As can be seen, all the diffractograms show a broad peak at about 25°, associated to the (200) facet of the hexagonal graphite structure, and five diffraction peaks at approximate angles of 40, 47, 67, 82, and 87°, associated to the (111), (200), (220), (311), and (222) facets, respectively, of Pt face-centered cubic (FCC) crystalline structure [25]. The (111) reflections of Pt crystalline structure were used to calculate the average crystallite sizes, whose values are listed in Table 2. All the prepared materials present crystallite sizes in the nanometric range (2–4 nm). However, the monometallic Pt/C catalyst shows a higher crystal size than the bimetallic materials. Hence during the formation of the crystallites, Cu (or copper oxide) exerts a protective role, leading to a smaller growth of the embryos formed during the

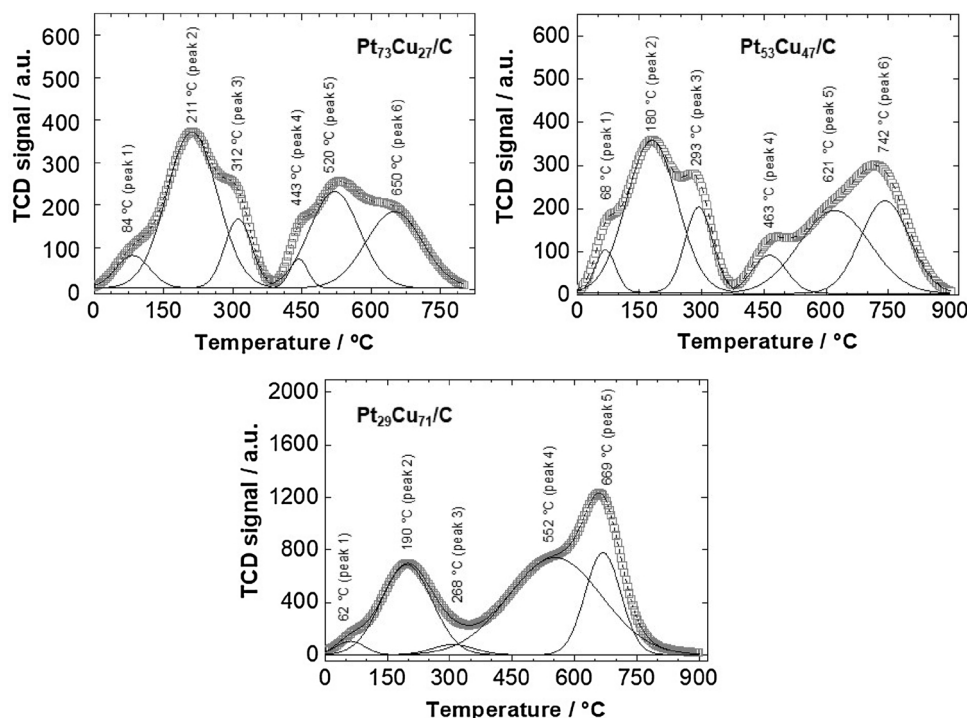


Fig. 4. TPR profiles of the different bimetallic electrocatalysts prepared.

drastic reduction induced by the hydrazine. The diffractograms also evidenced a shift of the peaks relative to Pt (FCC) phase to higher angles compared to those of the Pt/C electrocatalyst, indicating the formation of PtCu alloy [26,27]. Vegard's law can be applied to the PtCu bimetallic system [27–30] according to Eq. (3), where  $a_{PtCu}$  represents the lattice parameter of the bimetallic material,  $a_{Pt}$  the lattice parameter of Pt (0.3912 nm),  $a_{Cu}$  the lattice parameter of Cu (0.3601 nm), and  $x_{Cu}$  the Cu fraction in the PtCu alloy.

$$a_{PtCu} = x_{Cu}a_{Cu} + (1 - x_{Cu})a_{Pt} \quad (3)$$

From Eq. (2), the Cu fraction in the alloy can be estimated along with the percentage of deposited Cu that is actually alloyed with Pt. For this purpose, Eq. (4) must be applied, where  $Cu_{alloyed}$  is the amount of Cu in the alloy as a percentage of the total amount of Cu,  $x$  is the fraction of copper in the  $Pt_{1-x}Cu_x$  alloy, and Cu/Pt is the actual atomic ratio between the two metals.

$$Cu_{alloyed} = \frac{x_{Cu}}{(1 - x_{Cu})\left(\frac{Cu}{Pt}\right)} \quad (4)$$

The corresponding Cu fraction in the alloy and percentage of Cu alloyed are listed in Table 2. As observed, the Cu fraction in the PtCu alloy increases in the sequence from  $Pt_{73}Cu_{27}$  to  $Pt_{53}Cu_{47}$ . The larger fraction of Cu in the catalyst formulation favors a higher Cu insertion in the Pt FCC structure. Oppositely, the  $Pt_{29}Cu_{71}/C$  shows a decrease in the degree of alloying. A possible explanation for this may be the catalytic role that Pt could play in favoring the Cu(II) reduction and incorporation in the alloy [31]. Indeed, a large fraction of non-alloyed Cu [segregated amorphous metal or copper (I and/or II) oxides] is present in the  $Pt_{29}Cu_{71}/C$  catalyst. In the other two formulations, the fraction of alloyed Cu remains almost the same, corroborating the important role of the Pt nuclei in forming the PtCu alloy. Higher fractions of alloyed Cu may be achieved by using other reducing agents such as borohydride or by studying the influence of the reduction conditions such as the temperature, reduction time, and/or reducing agent concentration, among others. Moreover, alternative reduction routes, such as the thermal one, may be promising.

Fig. 2 shows the TEM images of the different electrocatalysts and the

corresponding particle size distribution. The average particle sizes are listed in Table 2. As can be observed, although the crystallite domains estimated by XRD are small, they tend to agglomerate, forming larger nanoparticles that are clearly visible in all the materials, leading to average particle sizes between 6 and 8 nm. Furthermore, the size distribution is rather heterogeneous (from 2 to 18–20 nm), although small particles can be seen in the high-resolution image obtained for the  $Pt_{53}Cu_{47}/C$  (2–4 nm, Fig. 2e). The use of a strong reducing agent such as hydrazine may be responsible for these results, which suggests that a capping agent would be necessary to prepare electrocatalysts with a more homogeneous particle size distribution when using the strong reducing agent hydrazine.

The surface composition and oxidation state of platinum and copper on the surface of the  $Pt_{73}Cu_{27}/C$ ,  $Pt_{53}Cu_{47}/C$ , and  $Pt_{29}Cu_{71}/C$  electrocatalysts were investigated using XPS. The respective spectra are displayed in Fig. 3 and the estimated Pt and Cu percentages in the surface are listed in Table 3. The Pt 4f XPS spectra show the Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> peaks for metallic platinum at approximately 71.3 and 74.7 eV, respectively. The Pt spectra also display three peaks at approximately 72.5, 75.5, and 77.4 eV, associated with electronic transitions of 4f electrons of PtO, Pt(OH)<sub>2</sub>, and PtO<sub>2</sub> species [32–34]. One interesting feature observed in the Pt 4f spectra is the appearance of a more intense signal in the region of highest energy (78–82 eV), where the Cu fraction is higher. A tentative assignment would be the Cu 3p<sub>1/2</sub> signal of the copper oxide [35], in consonance with the greater presence of this species. An estimation of the ratio of metallic to oxidized Pt reveals that the amount of metallic Pt remains almost constant in the  $Pt_{73}Cu_{27}/C$  and  $Pt_{53}Cu_{47}/C$ , whereas Pt oxide species are predominant in the  $Pt_{29}Cu_{71}/C$ , in which the presence of a larger amount of copper oxides species may induce the formation of surface PtO<sub>x</sub> sites. Finally, a very interesting feature observed in the Pt 4f spectra is the downshift of the Pt 4f<sub>7/2</sub> (71.4 eV for  $Pt_{73}Cu_{27}/C$ , 71.1 eV for  $Pt_{53}Cu_{47}/C$ , and 71.5 eV for  $Pt_{29}Cu_{71}/C$ ) for the most alloyed electrocatalysts, evidencing an electronic effect of Cu on the sites of the outermost Pt layers. Regarding the Cu 2p spectra,  $Pt_{73}Cu_{27}/C$  shows tiny peaks at approximately 932 and 952 eV, attributed to metallic copper or cuprous oxide, along with a weak satellite signal ascribed to the presence of small amounts of cupric

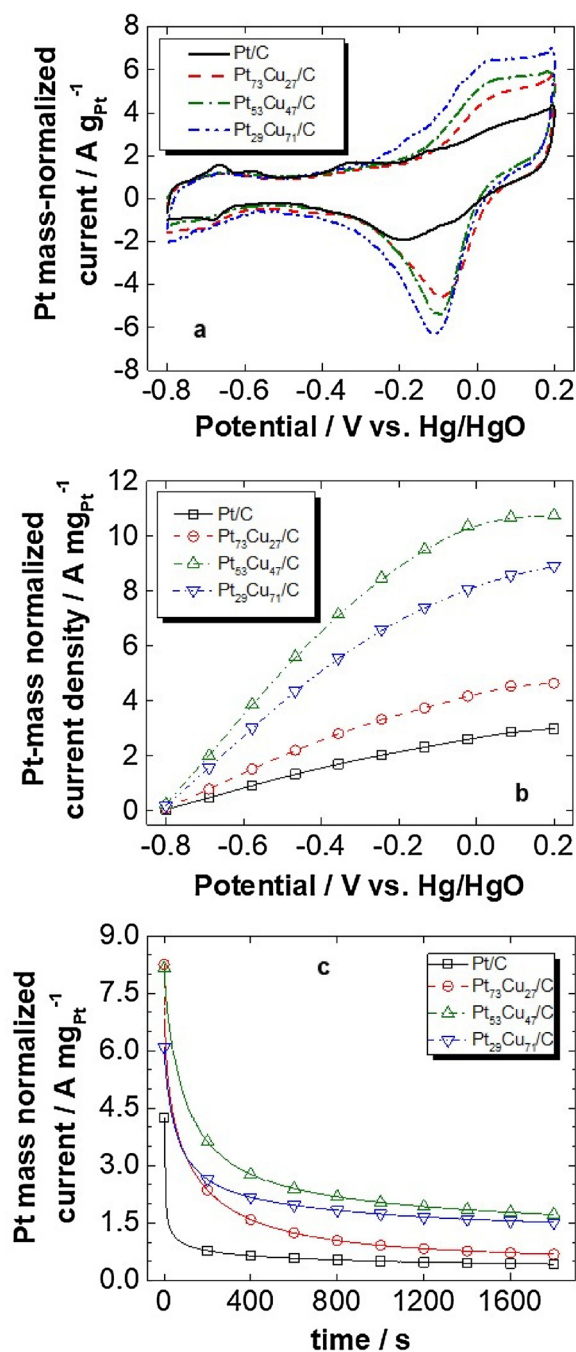


Fig. 5. a) Cyclic voltammograms of the different electrocatalysts in 1 mol L<sup>-1</sup> KOH; b) linear sweep voltammograms in 1 mol L<sup>-1</sup> KOH and 1 mol L<sup>-1</sup> hydrazine hydrate; and c) chronoamperograms at 0.024 V vs Hg/HgO in 1 mol L<sup>-1</sup> KOH and 1 mol L<sup>-1</sup> hydrazine hydrate.

oxide [27,28,36,37]. These peaks become more evident in the Pt<sub>53</sub>Cu<sub>47</sub>/C material, at 934 and 954 eV, in addition to the satellites at 943 and 963 eV. The strongest evidences of the presence of CuO are observable in the Pt<sub>29</sub>Cu<sub>71</sub>/C. Hence, the higher the fraction of Cu, the larger the tendency to form copper oxide species, whose presence may induce the larger fraction of surface Pt oxides.

Table 3 also lists the Pt:Cu surface composition. As can be seen, a comparison between the actual ratio of metals and the surface one reveals a certain enrichment of Pt. This result may be explained in terms of a possible galvanic displacement of the nanometallic copper nanoparticles formed during the reduction process by the Pt precursor [38]. Metallic copper then transforms into Cu(II) species. The higher the Cu

content in the catalyst formulation, the more severe this phenomenon would be, which could explain the more prominent CuO peaks observed in the XPS spectra. Furthermore, soluble Cu<sup>2+</sup> could be formed, which would support the reduction of the metallic content observed in the EDX results at a higher Cu fraction in the catalyst formulation and greater Pt enrichment in the catalyst surface.

Fig. 4 shows the TPR signals of the Pt<sub>73</sub>Cu<sub>27</sub>/C, Pt<sub>53</sub>Cu<sub>47</sub>/C, and Pt<sub>29</sub>Cu<sub>71</sub>/C electrocatalysts. As can be observed, all the materials present an initial reduction peak (peak 1) at low temperature (60–80 °C). This temperature relatively low compared to others reported in the literature for Pt/C catalysts (in the range of 100–200 °C [39–42]). This peak is attributed to the reduction of surface platinum oxides. Subsequently, a larger peak (peak 2) appears in the range of 180–210 °C for all the materials. This peak can be ascribed to the mixed reduction of both metals in the PtCu alloy [43,44]. Furthermore, this peak can contain a contribution from copper oxides, which are reduced at lower temperature (approx. 200 °C) in the presence of Pt [41]. Furthermore, the most alloyed electrocatalyst possesses the lowest temperature for the maximum in the signal compared to the other catalysts, corroborating that the Pt can exert a spillover effect on copper oxides. The third and fourth peaks in the first low-temperature region of the TPR profiles appear in the ranges of 290–310 °C and 440–460 °C in the Pt<sub>73</sub>Cu<sub>27</sub>/C and Pt<sub>53</sub>Cu<sub>47</sub>/C catalysts. According to the literature [43] (and in agreement with the XPS spectra), those peaks may be assigned to the reduction of Cu<sub>2</sub>O and CuO species that are not interacting with Pt. It is interesting to note that in the Pt<sub>53</sub>Cu<sub>47</sub>/C, the area of the peaks is larger (a larger Cu fraction), although their proportions are similar. Thus it can be speculated that, in percentage terms, the copper speciation is similar in both materials. Finally, two large peaks can be observed above 500 °C (peaks 5 and 6 of Pt<sub>73</sub>Cu<sub>27</sub>/C and Pt<sub>53</sub>Cu<sub>47</sub>/C). These can be ascribed to gasification of the carbon support [39], even though large Cu<sub>2</sub>O/CuO particle sizes may also contribute to the lowest temperature peak [45]. In the case of the Pt<sub>29</sub>Cu<sub>71</sub>/C, a very weak peak can be identified at 268 °C (peak 3) and is tentatively assigned to a small amount of cuprous oxide. The fourth peak, centered at 552 °C, may contain a simultaneous contribution from the predominant cupric oxide and support gasification. The final peak (peak 5, > 650 °C) is assigned to gasification of the carbon support. A very interesting feature of the TPR profiles is the increase observed in the TCD signal as the Cu fraction in the electrocatalysts increases, with special significance in the case of the Pt<sub>29</sub>Cu<sub>71</sub>/C, confirming the larger amount of oxidized species deposited on the carbon support.

Fig. 5a displays the corresponding cyclic voltammograms in alkaline medium (1 mol L<sup>-1</sup> KOH) of Pt/C and the PtCu/C electrocatalysts. As can be seen, the profiles of the PtCu/C electrocatalysts do not show the characteristic anodic stripping peaks associated with the hydrogen adsorption/desorption on Pt surface atoms (–0.8 to –0.5 V vs. Hg/HgO) typical of Pt/C. This is a consequence of inhibition of the hydrogen adsorption/oxidation processes over Pt and can be attributed to the incorporation of copper within the structure of platinum on the PtCu/C electrocatalyst surfaces [46]. Also, the PtCu/C electrocatalysts show an increase in the currents in the double layer (–0.55 and 0.3 V vs. Hg/HgO) with increasing copper content, which is ascribed to the growing presence of copper oxides [47–49]. Finally, larger currents are observed in the regions of Pt-oxide formation/reduction, whose intensification is due to important contributions from copper redox pairs [50]. This feature becomes more evident at the higher Cu fraction as a result of the more Cu-enriched surface.

The electrochemical activity towards H<sub>2</sub>EO is assessed by LSV. Fig. 5b displays the corresponding profiles. As can be observed, the H<sub>2</sub>EO activity improves notably when Cu is added to the catalyst formulation. In the literature [51,52], the formation of a PtCu alloy leads to a reduction of the unfilled Pt 5d states, lowering the adsorption strengths (of the eventual adsorbates formed) compared to Pt [53] and diminishing the tendency to form platinum oxide at high potential. Two pieces of evidence can support this statement: the lower binding energy



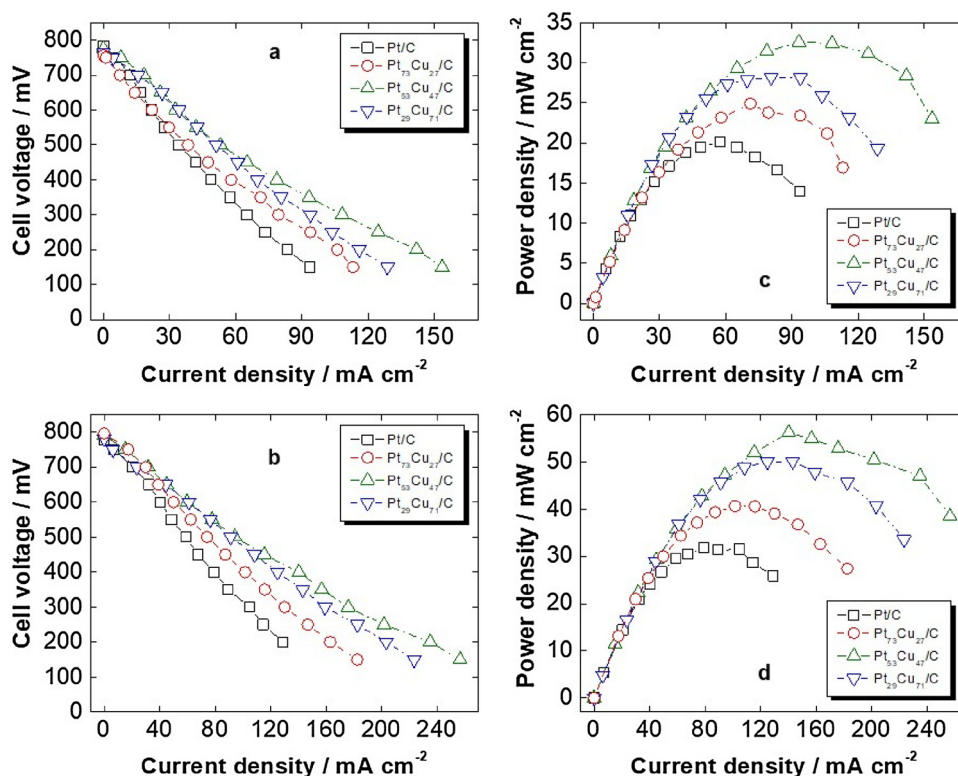


Fig. 6. Polarization curves at: a) 60 °C and b) 80 °C; power density curves at c) 60 °C and d) 80 °C for the different electrocatalysts.

Table 4

Maximum power density (MPD) values obtained from the power density curves in a single DHFC operating at 60 and 80 °C for Pt/C and PtCu/C electrocatalysts and percentage variation of the MPD of the PtCu/C electrocatalysts in relation to the Pt/C.

Electrocatalyst	DHFC at 60 °C		DHFC at 80 °C	
	MPD (mW cm <sup>-2</sup> )	PI	MPD (mW cm <sup>-2</sup> )	PI
Pt/C	20.1	–	31.5	–
Pt <sub>73</sub> Cu <sub>27</sub> /C	24.9	23.4	40.7	29.2
Pt <sub>53</sub> Cu <sub>47</sub> /C	32.6	62.2	56.1	78.1
Pt <sub>29</sub> Cu <sub>71</sub> /C	28.2	40.3	50.1	59.0

observed for the Pt<sub>57</sub>Cu<sub>47</sub>/C in the Pt 4f<sub>7/2</sub> region of the XPS spectra and the lower reduction temperature of Pt oxide species in the bimetallic materials. These features are indeed important. According to the literature [20], non-oxidized Pt sites are required for complete H<sub>2</sub>EO, where dissociative adsorption [20,54–56] takes place in order to produce adsorbed N<sub>2</sub>H<sub>x,ads</sub> and H<sub>ads</sub> species that are subsequently oxidized by adsorbed OH<sub>ads</sub> and/or OH<sup>-</sup>. The lower tendency to form Pt oxides in the alloyed PtCu along with the expected weaker adsorption strength can intrinsically accelerate the H<sub>2</sub>EO dissociative adsorption steps on Pt (electronic effect). On the other hand, the presence of oxidized copper species may contribute, through the bifunctional mechanism, by providing OH<sub>ads</sub> species after OH<sup>-</sup> discharge. Finally, copper/copper oxide species are active for H<sub>2</sub>EO, as stated in the Introduction. The combination of all these factors explains the enhanced electrochemical performance of the PtCu electrocatalysts. Regarding the composition, the most adequate (balanced) material is the almost equiatomic Pt<sub>53</sub>Cu<sub>47</sub>/C, in which almost half of the copper forms, with Pt, the most alloyed electrocatalyst in combination with an optimum amount of surface copper/copper oxides. In the Pt<sub>73</sub>Cu<sub>27</sub>/C, the lower degree of alloying attained and the reduced presence of copper diminish the electrochemical performance. The Pt<sub>29</sub>Cu<sub>71</sub>/C also presents a lower degree of alloying and a high fraction of Cu species on the catalytic

surface, limiting its performance. The presence of the active copper phase may reduce the size of the observed performance drop compared to Pt<sub>73</sub>Cu<sub>27</sub>/C. The chronoamperometric curves shown in Fig. 5c confirm these results.

Fig. 6a and b show the polarization curves, while Fig. 6c and d display the power density curves in a single DHFC operating at 60 and 80 °C, using Pt<sub>73</sub>Cu<sub>27</sub>/C, Pt<sub>53</sub>Cu<sub>47</sub>/C, Pt<sub>29</sub>Cu<sub>71</sub>/C, and Pt/C electrocatalysts as anodes. As can be observed, the polarization curves confirm that, regardless of the temperature, the Pt<sub>53</sub>Cu<sub>47</sub>/C is the most active material with the highest current densities, as seen in the three-electrode glass cell. These results are also corroborated by the power densities at 60 and 80 °C. Table 4 lists the maximum power densities (MPDs) and performance improvements (PIs) with respect to the Pt/C electrocatalyst, and it can be seen that the highest values were found for the Pt<sub>53</sub>Cu<sub>47</sub>/C. In this material, it is possible to achieve the maximum fraction of PtCu alloy with the optimum fraction of copper oxides present in the surface. The lower degree of alloying of the other two PtCu electrocatalysts and, particularly, the reduced amount of copper/copper oxides in the Pt<sub>73</sub>Cu<sub>27</sub>/C explain the observed sequence Pt<sub>53</sub>Cu<sub>47</sub>/C > Pt<sub>29</sub>Cu<sub>71</sub>/C > Pt<sub>73</sub>Cu<sub>27</sub>/C > Pt/C. Finally, it is interesting to observe that the PI becomes stronger as the temperature increases. This could be explained by the activation of the Cu phase, which reinforces the auxiliary effects discussed extensively above. Thus, the potential to reduce noble metal loading in this application is consistent with other studies such as [57,58], which also show potential for high-performance DHFC technology utilizing either low- or non-noble metal electrocatalysts.

#### 4. Conclusions

This study demonstrates the promotional effect of copper on the electrocatalytic activity for H<sub>2</sub>EO of platinum. The formation of a PtCu alloy seems to alter the electronic environment favorably and is balanced by the presence of Cu oxide species that can donate OH<sub>ads</sub> for completion of the H<sub>2</sub>EO, leading to a very active material for

application in DHFCs. Despite some particle agglomeration due to the use of hydrazine as a strong reducing agent, the different highly electroactive  $\text{Pt}_x\text{Cu}_{100-x}/\text{C}$  electrocatalysts outperform the reference Pt/C (also prepared by CRH). Regarding the Pt:Cu ratio, the highest performance is achieved with the almost equiatomic  $\text{Pt}_{53}\text{Cu}_{47}/\text{C}$ , whose electrocatalytic surface attains an optimum equilibrium between the largest fraction of Cu alloyed with Pt and the presence of active copper oxides. A lower Cu content in the catalyst formulation reduces the degree of alloying and especially the fraction of copper oxides. A higher Cu content also reduces the degree of alloying in these materials prepared by CRH, reducing the electronic effect despite the larger fraction of copper oxides. In this scenario, the electrochemical performances studied in a more fundamental glass cell and in an actual single DHFC lead to the following sequence of electroactive materials for HYE:  $\text{Pt}_{53}\text{Cu}_{47}/\text{C} > \text{Pt}_{29}\text{Cu}_{71}/\text{C} > \text{Pt}_{73}\text{Cu}_{27}/\text{C} > \text{Pt}/\text{C}$ .

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